High-Resolution X-Ray Spectroscopy by Microcalorimetry

High-resolution x-ray spectroscopy shows up as a need in both government and industrial contexts. In the field of Homeland Security, there is an identified need for rapid forensic identification of chemical compounds that may be explosive or toxic. In the industrial sector, the semiconductor industry has identified the current resolution of silicon x-ray detectors as an impediment in the use of electron microscopes to analyze chemical problems in the development or production of new semiconductors. A new type of detector of x-ray fluorescence spectra has been a measurement need for some time. The Transition Edge Sensor Microcalorimeter detector invented at NIST appears to be a potential solution to these requirements.

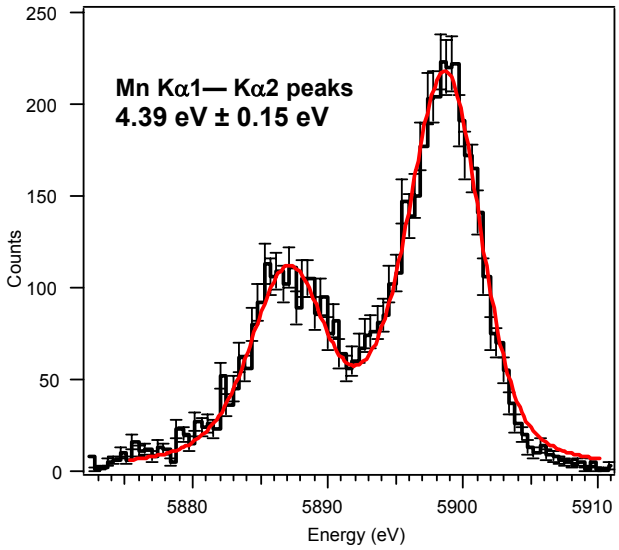
T.J. Jach, J.A. Small, R.L. King, (Div. 837)
J. Ullom (EEEL)

NIST's Transition Edge Sensor Microcalorimeter detector combines relatively high resolution of the detected x-rays with a broad detection spectrum. The detector has shown initial promise, but also suffers problems typical of a major paradigm shift in a technology. Various technical problems associated with operation as an ultracold detector using complex superconducting electronics cause instability, degraded resolution, and nonlinearity in the spectra. Beyond that, there are questions about the actual conditions of obtaining spectra, the stability of chemical compounds while the spectra are being obtained, and the nature of features in the fluorescence emission process that can be identified with a detector of the projected resolution.

In cooperation with J. Ullom (EEEL) we have been addressing these issues and have achieved several critical advances. Additional collaboration with T. Elam (U. of Washington) and E. Shirley (PL) were formed to address the questions about fluorescence emission from chemical compounds. The research builds on the work that was identified last year as improving the stability of the thermal operating point of the detector. This year we made progress in the following directions: a) intrinsic resolution of the detector, b) identification of chemical compounds which could be identified with the detector, and c) incorporating the detector into a dedicated instrument for research purposes.

The first activity involved improving the resolution of the detector. As of last fiscal year, the detector was improved to be capable of 11 eV to 12 eV resolution over extended periods of time. During the first half of this year, we installed a new microcalorimeter head developed at NIST Boulder which improved the resolution considerably. We demonstrated a resolution of 4.4 eV at 6 keV. This performance is shown in the figure below.

Microcalorimeter spectrum of Mn K radiation, showing the resolution of the $K\alpha_1$-$K\alpha_2$ peaks (separation 11 eV).

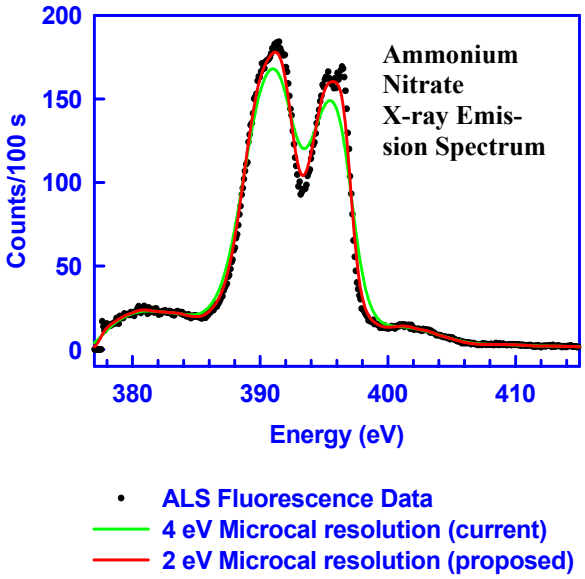


The improved resolution is already sufficient to identify not only specific elements by their x-ray fluorescence emission, but also chemical phase information based on the chemical bonding environment.

As a test case, we selected nitrogen compounds, in which the excited state of a 1s core hole is directly filled with valence electrons—2s and 2p electrons from the N atom, as well as valence electrons from other atoms in the compound. The hybridization of these atomic states into molecular orbitals results in a valence electron density of states that extends over approximately 30 eV. The resulting emission spectra extend over a similar energy width.

In collaboration with W. MacCrehan (839), we identified a series of nitrogen compounds representing a broad range of chemical bonding situations. We proceeded to take x-ray fluorescence spectra of these compounds with a high-resolution grating spectrometer excited by tuned x-rays on a beamline at the Advanced Light Source (ALS) at the Lawrence Berkeley Laboratory. The resulting spectra confirmed that there were variations in the x-ray emission that are specific to the chemical phase of the compounds and could be identified at the current resolution level of the

microcalorimeter detector. The figure below illustrates the nitrogen emission spectrum we obtained with 0.5 eV resolution at the ALS from ammonium nitrate, an explosive compound. Superimposed on it are curves which illustrate the spectral features as they would appear with a microcalorimeter detector with 2 eV resolution (a future improvement) and 4 eV (a current possibility). The peaks related to the chemical phase are definitely identifiable in the emission spectrum at the current level of resolution.



The graph is an X-ray emission spectrum of ammonium nitrate taken with a grating spectrometer (resolution 0.5 eV) at the Advanced Light Source. A convolution with 4 eV and 2 eV instrument functions shows the level of current and possible future resolution of the microcalorimeter detector.

In 2005, the innovative microcalorimeter detector was incorporated into a dedicated, refurbished, JEOL 840 electron microprobe.

The availability of the dedicated instrument has already permitted development work on vacuum windows allowing the transmission of low-energy x-rays and on sample holders allowing the optimum excitation and detection of x-rays.

Impact: NIST has been working with an ATP-funded company on the commercial production of microcalorimeter detector. Improvements which have been described last year and this year are being incorporated into the company's instrument design. The ability of the microcalorimeter detector to provide chemical speciation in an electron probe environment, if realized, would represent a significant advancement in the analytical capabilities of this widely used instrument.

Future Plans: Our first requirement is to obtain optimum operating conditions of the microcalorimeter detector in conjunction with the electron microprobe. This will be demonstrated by x-ray emission spectra which can be proven to give an accurate quantitative analysis of the elements present.

Publications:

T.J. Jach, J.A. Small, and D.E. Newbury, **"Improving Energy Stability in the NIST Microcalorimeter X-ray Detector",** *Powder Diffraction* **20**, 134 (2005).

T.J. Jach, J.A. Small, and D. E. Newbury, **"Improving Energy Stability in the NIST Microcalorimeter X-ray Detector,"** *Adv. X-ray Anal*. **48**, 216 (2005).